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(71) Applicant(s)
The Goodyear Tire & Rubber Company
(Incorporated in USA - Ohio)
1144 East Market Street, Akron, Ohio 44316-0001,
United States of America

(72) Inventor(s)
Manoj Ajbani
Wen-Liang Hsu
Adel Farhan Halasa
Ginger Lee
Eric Sean Castner

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(56) Documents Cited
GB 0848754 A
EP 0551532 A
JP 550062269 A
JP 2000159960 A
US 5576373 A
US 4889885 A
US 3973071 A
US 2885381 A

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(74) Agent and/or Address for Service
Carpmaels & Ransford
43 Bloomsbury Square, LONDON, WC1A 2RA,
United Kingdom

(54) Abstract Title
Lightweight rubber composition containing clay

(57) This invention relates to a light weight rubber blend that can be beneficially used in rubber articles, such as power transmission belts and tires. In the rubber blends of this invention a 2:1 layered silicate clay, preferably an organophilic 2:1 layered silicate clay, is substituted for a portion of the carbon black that is normally used in the rubber as a filler. This can be done without sacrificing the physical properties of the rubber composition in cases where the rubber in the blend contains an amino group. Tire tread compounds that utilize such rubber compositions offer increased vehicle fuel economy. This invention also relates to improving the strength, modulus and elongation of carbon black and silica filled compounds by the addition of 2:1 layered silicate clays thereto without modifying the level of carbon black or silica. Such compounds have increased flexibility and tensile strength for tire side-wall applications and improved traction and cornering performance in tire treads. This invention more specifically discloses a light weight rubber composition that is comprised of: (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, (2) from about 0.1 phr to about 25 phr of a 2:1 layer type silicate clay, and optionally (3) a silica coupling agent. The present invention further discloses a tire which is comprised of a generally toroidal-shaped carcass with an outer circumferential tread, two spaced beads, at least one ply extending from bead to bead and sidewalls extending radially from and connecting said tread to said beads; wherein said tread is adapted to be ground-contacting; wherein the tread is comprised of the rubbery polymer of this invention.

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LIGHT WEIGHT RUBBER COMPOSITION CONTAINING CLAY

Background of the Invention

Tires are increasingly expected to provide higher and higher levels of performance characteristics. For instance, it is normally expected for tires to exhibit good traction characteristics on both dry and wet surfaces as well as low rolling resistance for good vehicle fuel economy. However, it has traditionally been very difficult to improve the traction characteristics of a tire without compromising its rolling resistance and treadwear. Low rolling resistance is important because good fuel economy is virtually always an important consideration. Reducing the weight of tires is also a goal of automobile and truck manufacturers because reduced weight results in improved fuel economy. Reducing the weight of tires is of particular importance in the case of aircraft tires. Good treadwear is also an important consideration because it is generally the most important factor in determining the life of the tire.

The traction, treadwear and rolling resistance of a tire is dependent to a large extent on the dynamic viscoelastic properties of the elastomers utilized in making the tire tread. In order to reduce the rolling resistance of a tire, rubbers having a high rebound have traditionally been utilized in making the tire's tread. On the other hand, in order to increase the wet skid resistance of a tire, rubbers that undergo a large energy loss have generally been utilized in the tire tread. In order to balance these two viscoelastically inconsistent properties, mixtures of various types of synthetic and natural rubber are normally utilized in tire treads. For instance, various mixtures of styrene-butadiene rubber and polybutadiene rubber are commonly used as a rubber material for automobile tire treads. However, such blends are not totally satisfactory for all purposes.

Rubbers having intermediate glass transition temperatures (-70°C to -40°C) compromise rolling resistance and treadwear without significantly increasing traction characteristics. For this reason, blends of rubbers having low glass transition temperatures and rubbers having high glass transition temperatures are frequently utilized to attain improved traction characteristics without significantly compromising rolling resistance or treadwear. However, such blends of rubbers having low glass transition temperatures and rubbers having high glass transition temperatures exhibit poor processability. This major disadvantage associated with such blends has greatly hampered their utilization in making tire tread compounds.

United States Patent 2,885,381 discloses a composition of matter comprising a copolymer of a conjugated diene and a heterocyclic nitrogen containing monomer having a sole CH_2=CH- substituent, such as 2-vinylpyridine, said copolymer having been compounded with 25-100 weight parts per 100 parts of said copolymer of a finely ground mineral pigment selected from the group consisting of silica and aluminum silicate as the sole reinforcing agent.

In recent years, there has been a trend to include silica as a filler in tire tread compounds to further improve traction characteristics. United States Patent 5,036,133 discloses a vulcanizable rubber composition that is comprised of: (A) an uncured natural or synthetic isoprene rubber, or one or more uncured butadiene-based synthetic rubbers, or uncured blends thereof, said uncured rubbers being sulfur vulcanizable, (B) a silica filler, (C) sulfur, (D) an organic accelerator and (E) a vinylpyridine-butadiene interpolymer co-activator, said interpolymer co-activator (E) containing from about 20 percent to about 65 percent by weight of vinylpyridine units, the amount of said vinylpyridine-butadiene copolymer co-activator being from about 0.5 to 2 parts by weight per 100 parts by weight of said rubber.

Summary of the Invention

This invention relates to a rubber composition that can be used to reduce the weight of rubber articles, such as tires and power transmission belts, without compromising performance characteristics. For instance, the rubber composition of this invention can be utilized in manufacturing tires having reduced weight without compromising the rolling resistance or traction characteristics of the tire. This invention also relates to improving the strength, modulus and elongation of carbon black and silica filled compounds by addition of 2:1 layered silicate clays thereto without modifying the level of carbon black or silica. Such compounds have increased flexibility for tire side-wall applications with enhanced tensile strength and improved traction and cornering performance in tire treads. The rubber compositions of this invention are a blend of (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, (2) from about 0.1 phr to about 25 phr of a 2:1 layered silicate clay, preferably an organophilic 2:1 layered silicate clay, and optionally (3) a silica coupling agent. The rubber compositions of this invention will also typically contain from about 5 phr to about 100 phr of carbon black and optionally silica.

This invention more specifically discloses a rubber composition that is comprised of: (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, and (2) from about 0.1 phr to about 25 phr of a 2:1 layered silicate clay.

The present invention further discloses a tire which is comprised of a generally toroidal-shaped carcass with an outer circumferential tread, two spaced beads, at least one ply extending from bead to bead and sidewalls extending radially from and connecting said tread to said beads; wherein said tread is adapted to be ground-contacting; wherein the tread is comprised of: (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, (2) from about 0.1 phr to about 25 phr of a 2:1 layered silicate clay, and (3) a silica coupling agent.

Detailed Description of the Invention

The light weight rubber compositions of this invention comprised of: (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, (2) from about 0.1 phr to about 20 phr of a 2:1 layered silicate clay, and (3) optionally, a silica coupling agent. The 2:1 layered silicate clay will preferably be an organophilic 2:1 layered silicate clay.

Preferably the rubber composition comprises (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from 0.5 weight percent to 10 weight percent of the monomer containing an amino group; (2) from 1 phr to 10 phr, preferably 1 phr to 7 phr, of an organophilic 2:1 layered silicate clay; and (3) a silica coupling agent present at a level which is within the range of 0.5 phr to 15 phr, preferably 1 phr to 5 phr.

Preferably the rubber composition comprises (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from 0.5 weight percent to 10 weight percent of the monomer containing an amino group; (2) from 1 phr to 10 phr of an organophilic 2:1 layered silicate clay and (3) a silica coupling agent , wherein the ratio of the silica coupling agent to the 2:1 layered silicate clay is within the range of 0.1:1 to 1.5:1.

The rubber composition may additionally comprise from 1 phr to 70 phr of silica.

The amino group containing monomer will typically also contain a vinyl group (CH_2=CH_2-). Some representative examples of the amino group-containing vinyl monomers include polymerizable monomers having at least one amino group selected from the group consisting of primary, secondary and tertiary amino groups in their molecules. Of these, tertiary amino group-containing vinyl monomers are particularly preferred. These amino group-containing vinyl monomers may be used either singly or in any combination thereof.

Examples of the primary amino group-containing vinyl monomers include acrylamide, methacrylamide, p-aminostyrene, aminomethyl (meth)acrylate, aminoethyl (meth)acrylate, aminopropyl (meth)acrylate and aminobutyl (meth)acrylate.

Examples of secondary amino group-containing vinyl monomers include anilinostyrenes; anilinophenylbutadienes; and N-monosubstituted (meth)acrylamides, such as N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-methylolacrylamide and N-(4-anilinophenyl) methacrylamide.

Examples of tertiary amino group-containing vinyl monomers include N,N-disubstituted aminoalkyl acrylates, N,N-disubstituted aminoalkyl acrylamides, N,N-disubstituted amino-aromatic vinyl compounds and vinyl compounds having a pyridyl group.

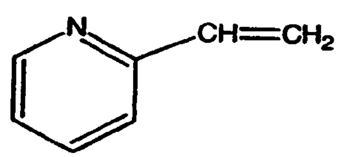
Examples of the N,N-disubstituted amino alkyl acrylates include esters of acrylic acid or methacrylic acid, such as N,N-dimethylaminomethyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-dimethylaminobutyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-diethylaminobutyl (meth)acrylate, N-methyl-N-ethylaminoethyl (meth)acrylate, N,N-dipropylaminoethyl (meth)acrylate, N,N-dibutylaminoethyl (meth)acrylate, N,N-dibutylaminopropyl (meth)acrylate, N,N-dibutylaminobutyl (meth)acrylate, N,N-dihexylaminoethyl (meth)acrylate, N,N-dioctylaminoethyl (meth)acrylate and acryloylmorpholine. Of these, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dipropylaminoethyl (meth)acrylate, N,N-dioctylaminoethyl (meth)acrylate and N-methyl-N-ethylaminoethyl (meth)acrylate.

Examples of the N,N-disubstituted aminoalkyl acrylamides include acrylamide compounds or methacrylamide compounds such as N,N-dimethylaminomethyl (meth)acrylamide, N,N-dimethylaminoethyl (meth)acrylamide, N,N-

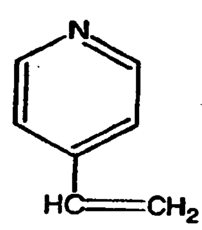
dimethylaminopropyl (meth)acrylamide, N,N-dimethylaminobutyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, N,N-diethylaminobutyl (meth)acrylamide, N-methyl-N-ethylaminoethyl (meth)acrylamide, N,N-dipropylaminoethyl (meth)acrylamide, N,N-dibutylaminoethyl (meth)acrylamide, N,N-dibutylaminopropyl (meth)acrylamide, N,N-dibutylaminobutyl (meth)acrylamide, N,N-dihexylaminoethyl (meth)acrylamide, N,N-dihexylaminopropyl (meth)acrylamide and N,N-dioctylaminopropyl (meth)acrylamide. Of these, N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide and N,N-dioctylaminopropyl (meth)acrylamide are preferred.

Example of the N,N-disubstituted amino-aromatic vinyl compounds include styrene derivatives such as N,N-dimethylaminoethylstyrene, N,N-diethylaminoethylstyrene, N,N-dipropylaminoethylstyrene and N,N-dioctylaminoethylstyrene.

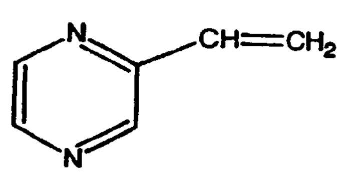
Examples of the pyridyl group-containing vinyl compounds include 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and 5-ethyl-2-vinylpyridine. Of these pyridyl group-containing vinyl monomers, 2-vinylpyridine which has the structural formula:



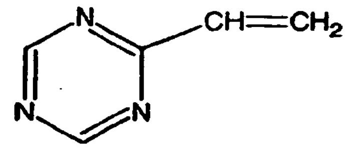
and 4-vinyl pyridine which has the structural formula:



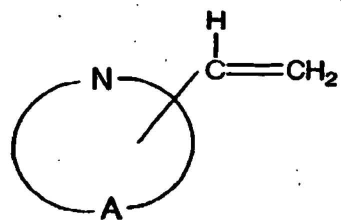
are preferred. The most preferred pyridyl group-containing monomer is 2-vinylpyridine. Amino group containing monomers that contain more that one amino group can be used. Some representative examples of such monomers include 2-vinyl pyrimidine which has the structural formula:



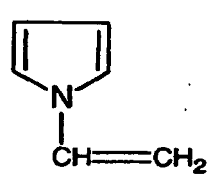
and 2-vinyl 1,3,5-triazine which has the structural formula:



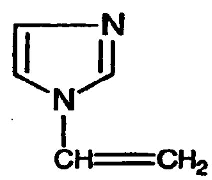
Heterocyclic amines having the structural formula:



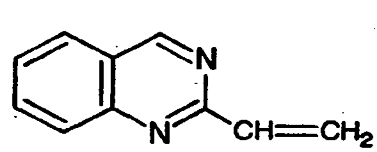
wherein A represents a -CH- group or a $-CH_2-$ group and wherein the heterocyclic amine is aromatic or aliphatic and derivatives thereof are in general a preferred class of amino group containing monomers. The amino group containing monomer can be an N-vinyl substituted pyrrole, an N-vinyl substituted 3-pyrroline, an N-vinyl substituted 4-(1-pyrrolidinyl) piperidine, an N-vinyl substituted imidazole, an N-vinyl substituted 1-(2-pyridyl)piperazine, or an N-vinyl substituted 1-(2-pyrimidyl) piperazine. For instance, the amino group containing monomer can be of the structural formula:



or



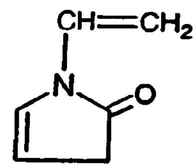
The amino group containing monomer can also contain more that one aromatic ring, such as vinyl substituted quinazoline, vinyl substituted quinaldine, or vinyl substituted quinoline. For instance, vinyl substituted quinazoline of the structural formula:



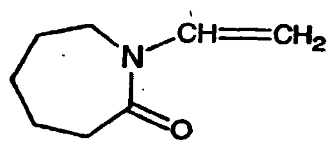
can be utilized as the amino group containing monomer. Vinyl group containing bicyclo amines can also be employed as the amino group containing monomer. For instance, the

amino group containing monomer can be a vinyl substituted 1,4-diazocycloheptane or a vinyl substituted 1,5-diazacyclooctane.

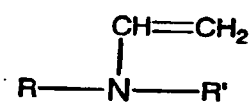
For economic reasons N-vinyl 2-pyrrolidone and N-vinyl caprolactam are desirable amino group containing monomers. N-vinyl 2-pyrrolidone has the structural formula:



and N-vinyl caprolactam has the structural formula:

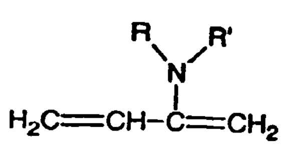
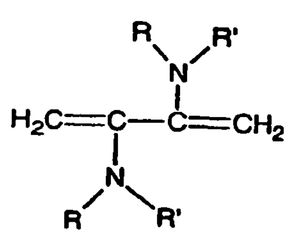
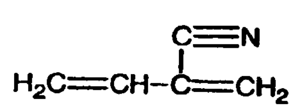


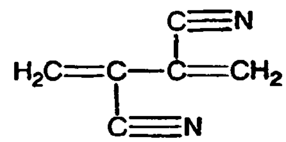
N-vinyl dialkyl amines are another class of amino group containing monomer that can be used. The N-vinyl dialkyl amines that can be used are typically of the structural formula:



wherein R and R' represent alkyl groups that can be the same or different. R and R' will typically represent alkyl groups that contain from 1 to about 10 carbon atoms. For instance the alkyl groups can be methyl groups, ethyl groups, n-propyl groups, iso-propyl groups, n-butyl groups, iso-butyl groups, or t-butyl groups. N-vinyl diisopropyl amine and N-vinyl diethylamine are representative examples of such amino group containing monomers. The alkyl groups will preferably contain from 1 to 4 carbon atoms.

The amino group containing monomer can also be a conjugated diolefin that is substituted with amino and/or cyano groups. Monomers of this type can be polymerized into the backbone of the amino group containing rubbery polymer. Some representative examples of such monomers include the following:

 ,  ,  and



wherein R and R' can be the same or different and represent alkyl groups that contain from 1 to about 10 carbon atoms. It is typically preferred for R and R' to represent alkyl groups that contain from 1 to about 4 carbon atoms.

The amino group containing rubber will typically contain from about 0.1 weight percent to about 20 weight percent of the amino group containing monomer. In other words, repeat units in the amino group containing rubber are derived from the amino group containing monomer. Generally, the repeat units derived from the amino group containing monomer differ from the amino group containing monomer in that double bonds are consumed as a result of the polymerization. In any case, it is normally preferred for the amino group containing rubber to contain from about 0.5 weight percent to about 10 weight percent of the amino group containing monomer. It is typically more preferred for the amino group containing rubber to contain from about 1 weight percent to about 4 weight percent of the amino group containing monomer.

In synthesizing the amino group containing rubber one or more conjugated diolefin monomers are copolymerized with the amino group containing monomer. The conjugated diolefin monomers which can be utilized in the synthesis of rubbery polymers generally contain from 4 to 12 carbon atoms. Those containing from 4 to 8 carbon atoms are generally preferred for commercial purposes. For similar reasons, 1,3-butadiene and isoprene are the most commonly utilized conjugated diolefin monomers. Some additional conjugated diolefin monomers that can be utilized include 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene, 2-phenyl-1,3-butadiene, and the like, alone or in admixture.

Other ethylenically unsaturated monomers, in addition to the amino group containing monomer, can also be copolymerized into the rubber. Some representative examples of additional ethylenically unsaturated monomers that can potentially be synthesized into the rubbery polymer include alkyl acrylates, such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, and the like; vinylidene monomers having one or more terminal CH_2=CH- groups; vinyl aromatics, such as styrene, α-methylstyrene, t-butylstyrene, bromostyrene, chlorostyrene, fluorostyrene, and the like;

α-olefins such as ethylene, propylene, 1-butene, and the like; vinyl halides, such as vinylbromide, chloroethane (vinylchloride), vinylfluoride, vinyliodide, 1,2-dibromoethene, 1,1-dichloroethene (vinylidene chloride), 1,2-dichloroethene, and the like; vinyl esters, such as vinyl acetate; α,β-olefinically unsaturated nitriles, such as acrylonitrile and methacrylonitrile; α,β-olefinically unsaturated amides, such as acrylamide, N-methyl acrylamide, N,N-dimethylacrylamide, methacrylamide, and the like.

Rubbery polymers which are copolymers of one or more diene monomers with one or more other ethylenically unsaturated monomers will normally contain from about 50 weight percent to about 99 weight percent conjugated diolefin monomers and from about 1 weight percent to about 50 weight percent of the other ethylenically unsaturated monomers in addition to the conjugated diolefin monomers. For example, copolymers of conjugated diolefin monomers with vinylaromatic monomers, such as styrene-butadiene rubbers which contain from 50 to 95 weight percent conjugated diolefin monomers and from 5 to 50 weight percent vinylaromatic monomers, are useful in many applications. In such cases, the rubber will, of course, also contain from 0.1 weight percent to 10 weight percent of the amino group containing monomer.

Vinyl aromatic monomers are probably the most important group of ethylenically unsaturated monomers which are commonly incorporated into polydiene rubbers. Such vinyl aromatic monomers are, of course, selected so as to be copolymerizable with the conjugated diolefin monomers being utilized. Generally, any vinyl aromatic monomer which is known to polymerize with organolithium initiators can be used. Such vinyl aromatic monomers typically contain from 8 to 20 carbon atoms. Usually, the vinyl aromatic monomer will contain from 8 to 14 carbon atoms. The most widely used vinyl aromatic monomer is styrene. Some examples of vinyl aromatic monomers that can be utilized include styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, α-methylstyrene, 4-phenylstyrene, 3-methylstyrene, t-butylstyrene, and the like.

The amino group containing rubber can be synthesized by emulsion polymerization, solution polymerization, vapor phase polymerization or bulk polymerization. The polymerization process can be conducted as a batch, semi-continuous, or continuous process. However, in solution polymerizations the amino group containing monomer will be added after substantially all of the other monomers have been incorporated into the rubbery polymer.

In many cases, it is preferred for the vinylpyridine containing rubbery polymer to be a vinylpyridine-styrene-butadiene terpolymer rubber. Such vinylpyridine-styrene-butadiene terpolymer rubbers will typically contain from about 0.5 weight percent to about 10 weight percent vinylpyridine, 0.5 weight percent to about 50 weight percent styrene and from about 50 weight percent to about 99 weight percent 1,3-butadiene. It is more preferred for the vinylpyridine-styrene-butadiene terpolymer rubbers to contain from about 1 weight percent to about 5 weight percent vinylpyridine, 5 weight percent to about 33 weight percent styrene and from about 66 weight percent to about 94 weight percent 1,3-butadiene. It is generally most preferred for the vinylpyridine-styrene-butadiene terpolymer rubbers to contain from about 1 weight percent to about 4 weight percent vinylpyridine, 10 weight percent to about 30 weight percent styrene and from about 82 weight percent to about 89 weight percent 1,3-butadiene.

The rubber compositions of this invention also contain from 0.1 phr (parts by weight per 100 parts by weight of rubber) to about 25 phr of an organophilic clay. It is typically preferred for the rubber compositions of this invention to contain from about 1 phr to about 10 phr of an organophilic clay. It is generally more preferred for the rubber compositions of this invention to contain from about 1 phr to about 7 phr of an organophilic clay. It is normally most preferred for the rubber compositions of this invention to contain from about 3 phr to about 6 phr of an organophilic clay.

The clays used in the practice of this invention are 2:1 layered silicate clays of the smectite, vermiculite and mica families. The 2:1 layered silicate clay can be synthetic or from a natural source. However, it should be understood that the 2:1 layered silicate clays used in the practice of this invention does not include talc. The 2:1 layered silicate clays that are typically preferred include montmorillonite, bentonite, hectorite, saponite, nontronite, beidellite, fluorohectorite, stevensite, volkonskoite, sauconite laponite, hallosite, related analogs thereof and their physical blends. Most preferably the 2:1 silicate clays are selected from the group consisting of smectite, montmorillonite, saponite, beidellite, hectorite, fluorohectorite, bentonite, nontronite, laponite, vermiculite, and hallosite. Clays that have been chemically modified to make them compatible with organic materials are preferred and are generally referred to as "organophilic" clays or "organo-clays". The basic starting material used to make organophilic clay is an exchangeable clay of the smectite group and can include montmorillonite (commonly known and mined as bentonite), hectorite, saponite, attapulgite and sepolite. These clays include exchangeable cationic species such as

sodium, potassium or calcium ions on their surface and between clay galleries or layers. In the course of manufacturing an organophilic clay, at least a portion of these exchangeable cationic species are substituted by an organic cation such as a quaternary amine, an organophosphorus ion, any other ion of the type known in the art as an oniumion, or the like. Some representative examples of surfactants that can be used include methyl tallow bis-2 hydroxy ethyl ammonium salt, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium salt, dimethyl benzyl hydrogenated-tallow ammonium salt, dimethyl dihydrogenated tallow ammonium salt, N-tallow alkyltrimethylene-diamine, hydrogenated tallow amine, octadecylamine, octadecylamine and gamma-aminopropyltriethoxy silane, polyoxyethylene decycloxypropylamine, n-dodecyl-pyrrolidone, or their combinations and analogs. Preferably the surfactant is selected from the group consisting of_methyl tallow bis-2-hydroxyethyl ammonium halides, methyl tallow bis-2-hydroxyethyl ammonium alkyl sulfates, methyl tallow bis-2-hydroxyethyl ammonium nitrate, methyl tallow bis-2-hydroxyethyl ammonium hydroxide, methyl tallow bis-2-hydroxyethyl ammonium acetate, methyl tallow bis-2-hydroxyethyl ammonium phosphate, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium halides, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium alkyl sulfates, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium nitrate, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium hydroxide, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium acetate, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium phosphate, dimethyl dehydrogenated-tallow ammonium halides, dimethyl dehydrogenated-tallow ammonium alkyl sulfates, dimethyl dehydrogenated-tallow ammonium nitrate, dimethyl dehydrogenated-tallow ammonium hydroxide, dimethyl dehydrogenated-tallow ammonium acetate, and dimethyl dehydrogenated-tallow ammonium phosphate. Quarternary ammonium surfactants, such as methyl tallow bis-2-hydroxyethyl ammonium chloride, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium methyl sulfate, and dimethyl dehydrogenated-tallow ammonium chloride, are most preferred. The addition of the organic group modifies the clay, making it compatible with organic compositions and in general allowing it to provide rheological modification in select organic fluids. The clay will typically be modified with up to about 70 parts by weight of the organic surfactant. The clay will more typically be modified with up to about 60 parts by weight of the surfactant and will preferably be modified with up to about 40 parts by weight of the surfactant.

There is a large body of prior art relating to the manufacture of organophilic clays. For example, United States Patent 2,531,427 and United States Patent 2,531,440 both disclose general processes for the manufacture of organically substituted clays. United States Patent 5,110,501 discloses a process for preparing organophilic clay in which the starting materials are reacted in a slurry under high shear. United States Patent 5,334,241, discloses a low moisture, direct addition process for the fabrication of organophilic clays. United States Patent 4,569,923 discloses yet another process for manufacturing organo-clays in which the clay is subjected to high energy pugmilling before reaction with the cation. The teachings of United States Patent 2,531,427, United States Patent 2,531,440, United States Patent 5,110,501, and United States Patent 5,334,241 are incorporated herein by reference in their entirety. In addition to processing parameters, the properties of an organophilic clay will depend upon the nature of the organic cation used for modification, as well as upon the amount of the cation incorporated into the clay. Specific modifiers are utilized for particular mixtures.

It has been found that the amount of organic cationic material that is incorporated into the clay will depend upon the particular technique used for its incorporation. The clays of interest have a generally lamellar structure, and the structure must be opened to some degree in order to permit the cation exchange reaction to take place. At the same time, care must be taken to avoid destroying the lamellar microstructure of the clay. One group of substitution techniques involves processing the clay in a slurry form, in which instance, solvation relaxes the clay's structure in order to permit penetration of the organic cations. While such techniques are effective, and widely employed, it is desirable to avoid such highly dilute reaction conditions since forming the slurry involves a time and space consuming step. Furthermore, dewatering of the finished product is energy-intensive. For this reason, low moisture, direct addition techniques as described in United States Patent 5,334,241, the disclosure of which is incorporated herein by reference in its entirety, are advantageously employed in the preparation of modified clays.

United States Patent 5,616,286 discloses a method for manufacturing an organophilic clay comprising the steps of: (1) providing a substantially non-slurried volume of a clay having an exchangeable cationic species; (2) providing a volume of a cationic organic material; (3) subjecting said non-slurried clay and said cationic material to a first stage reaction process wherein said clay and said cationic material are subjected to a confining pressure of at least 3,000 psi (2.07×10^7 Pa) while being mixed so that at

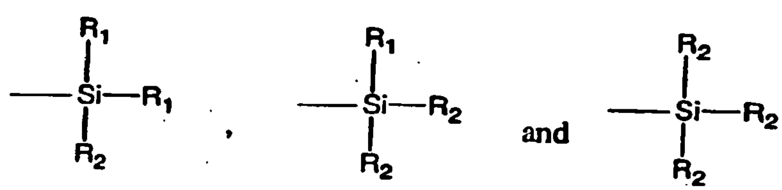
least some of the exchangeable cationic species in the clay arc substituted by said cationic material so as to provide a non-slurried first stage reaction mixture, which comprises an organically substituted clay which has some residual, exchangeable cationic species therein and some residual cationic material in a free form; and (4) subjecting said non-slurried first stage reaction mixture to a second stage reaction process wherein said mixture is subjected to a confining pressure of at least 8,000 psi ($5.52x10^7$ Pa) while being mixed so that at least some of the residual, exchangeable cationic species in the clay are substituted by said residual, cationic material. The teachings of United States Patent 5,616,286 are hereby incorporated herein by reference in their entirety.

The rubber compositions of this invention can optionally further contain about 0.5 phr to about 15 phr of a silica coupling agent. The rubber compositions of this invention will typically contain about 1 phr to about 5 phr of a silica coupling agent. The rubber compositions of this invention will preferably contain 2 phr to 4 phr of a silica coupling agent. The weight ratio of the silica coupling agent to the clay will typically be within the range of 0.1:1 to 1.5:1. The weight ratio of the silica coupling agent to the clay will preferably be within the range of 0.2:1 to 1.1:1. The weight ratio of the silica coupling agent to the clay will more preferably be within the range of 0.4:1 to 0.7:1.

The silica coupling agent is generally a sulfur containing organosilicon compound Examples of suitable sulfur-containing organosilicon compounds are of the formula:

$$\text{Z-Alk-Sn-Alk-Z} \qquad \text{(I)}$$

in which Z is selected from the group consisting of

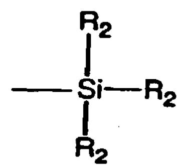


where R_1 is an alkyl group of 1 to 4 carbon atoms, cyclohexyl or phenyl; wherein R_2 is alkoxy of 1 to 8 carbon atoms or cycloalkoxy of 5 to 8 carbon atoms; and wherein Alk is a divalent hydrocarbon of 1 to 18 carbon atoms and n is an integer of 2 to 8.

Specific examples of sulfur-containing organosilicon compounds which may be used in accordance with the present invention include: 3,3'-bis(trimethoxysilylpropyl) disulfide, 3,3'-bis(triethoxysilylpropyl) tetrasulfide, 3,3'-bis(triethoxysilylpropyl)

octasulfide, 3,3'-bis(trimethoxysilylpropyl) tetrasulfide, 2,2'-bis(triethoxysilylethyl) tetrasulfide, 3,3'-bis(trimethoxysilylpropyl) trisulfide, 3,3'-bis(triethoxysilylpropyl) trisulfide, 3,3'-bis(tributoxysilylpropyl) disulfide, 3,3'-bis(trimethoxysilylpropyl) hexasulfide, 3,3'-bis(trimethoxysilylpropyl) octasulfide, 3,3'-bis(trioctoxysilylpropyl) tetrasulfide, 3,3'-bis(trihexoxysilylpropyl) disulfide, 3,3'-bis(tri-2'-ethylhexoxysilylpropyl) trisulfide, 3,3'-bis(triisooctoxysilylpropyl) tetrasulfide, 3,3'-bis(tri-t-butoxysilylpropyl) disulfide, 2,2'-bis(methoxy diethoxy silyl ethyl) tetrasulfide, 2,2'-bis(tripropoxysilylethyl) pentasulfide, 3,3'-bis(tricyclonexoxysilylpropyl) tetrasulfide, 3,3'-bis(tricyclopentoxysilylpropyl) trisulfide, 2,2'-bis(tri-2'-methylcyclohexoxysilylethyl) tetrasulfide, bis(trimethoxysilylmethyl) tetrasulfide, 3-methoxy ethoxy propoxysilyl 3'-diethoxybutoxy-silylpropyltetrasulfide, 2,2'-bis(dimethyl methoxysilylethyl) disulfide, 2,2'-bis(dimethyl sec.butoxysilylethyl) trisulfide, 3,3'-bis(methyl butylethoxysilylpropyl) tetrasulfide, 3,3'-bis(di t-butylmethoxysilylpropyl) tetrasulfide, 2,2'-bis(phenyl methyl methoxysilylethyl) trisulfide, 3,3'-bis(diphenyl isopropoxysilylpropyl) tetrasulfide, 3,3'-bis(diphenyl cyclohexoxysilylpropyl) disulfide, 3,3'-bis(dimethyl ethylmercaptosilylpropyl) tetrasulfide, 2,2'-bis(methyl dimethoxysilylethyl) trisulfide, 2,2'-bis(methyl ethoxypropoxysilylethyl) tetrasulfide, 3,3'-bis(diethyl methoxysilylpropyl) tetrasulfide, 3,3'-bis(ethyl di-sec. butoxysilylpropyl) disulfide, 3,3'-bis(propyl diethoxysilylpropyl) disulfide, 3,3'-bis(butyl dimethoxysilylpropyl) trisulfide, 3,3'-bis(phenyl dimethoxysilylpropyl) tetrasulfide, 3-phenyl ethoxybutoxysilyl 3'-trimethoxysilylpropyl tetrasulfide, 4,4'-bis(trimethoxysilylbutyl) tetrasulfide, 6,6'-bis(triethoxysilylhexyl) tetrasulfide, 12,12'-bis(triisopropoxysilyl dodecyl) disulfide, 18,18'-bis(trimethoxysilyloctadecyl) tetrasulfide, 18,18'-bis(tripropoxysilyloctadecenyl) tetrasulfide, 4,4'-bis(trimethoxysilyl-buten-2-yl) tetrasulfide, 4,4'-bis(trimethoxysilylcyclohexylene) tetrasulfide, 5,5'-bis(dimethoxymethylsilylpentyl) trisulfide, 3,3'-bis(trimethoxysilyl-2-methylpropyl) tetrasulfide, 3,3'-bis(dimethoxyphenylsilyl-2-methylpropyl) disulfide.

The preferred sulfur-containing organosilicon compounds are the 3,3'-bis(trimethoxy or triethoxy silylpropyl) sulfides. The most preferred compound is 3,3'-bis(triethoxysilylpropyl) tetrasulfide. Therefore, as to Formula I, preferably Z is



where R_2 is an alkoxy of 2 to 4 carbon atoms, with 2 carbon atoms being particularly preferred; Alk is a divalent hydrocarbon of 2 to 4 carbon atoms with 3 carbon atoms being particularly preferred; and n is an integer of from 3 to 5 with 4 being particularly preferred.

The rubber compositions of this invention will typically also contain carbon black as a filler. The carbon black will normally be utilized at a level of about 5 phr to about 100 phr. It is generally preferred for the carbon black to be employed at a level of about 25 phr to about 75 phr. It is desirable to substitute as much of the organophilic clay for carbon black as possible to reduce the weight (specific gravity) of the rubber composition to the greatest possible extent. In some cases, it will be beneficial to utilize a combination of silica and carbon black as the filler. It is to be appreciated that the silica coupler may be used in conjunction with a carbon black (namely, pre-mixed with a carbon black prior to addition to the rubber composition) and such carbon black is to be included in the aforesaid amount of carbon black for the rubber composition. Talc can also be included as a portion of the filler to reduce cost.

The commonly employed siliceous pigments used in rubber compounding applications can be used as the silica, including pyrogenic and precipitated siliceous pigments (silica), although precipitated silicas are preferred. The siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate; e.g., sodium silicate.

Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304 (1930).

The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300. The silica might be expected to have an average ultimate particle size, for

example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhone-Poulenc, with, for example, designations of Z1165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2 and VN3.

The rubbery compositions of this invention can be compounded utilizing conventional ingredients and standard techniques. For instance, the amino group containing rubbery polymer will typically be mixed with the silica coupling agent, the organophilic clay, optionally additional fillers, sulfur, accelerators, oils, waxes, scorch inhibiting agents and processing aids. The rubber compositions of this invention can also be blended with conventional rubbers, such as polybutadiene rubber, synthetic polyisoprene rubber, natural rubber, styrene-butadiene rubber (SBR), α-methylstyrene-butadiene rubber, α-methylstyrene-isoprene rubber, styrene-isoprene-butadiene rubber (SIBR), styrene-isoprene rubber (SIR), isoprene-butadiene rubber (IBR), α-methylstyrene-isoprene-butadiene rubber, and α-methylstyrene-styrene-isoprene-butadiene rubber. In most cases, the rubbery polymer will be compounded with sulfur and/or a sulfur-containing compound, at least one accelerator, at least one antidegradant, at least one processing oil, zinc oxide, optionally a tackifier resin, optionally a reinforcing resin, optionally one or more fatty acids, optionally a peptizer and optionally one or more scorch inhibiting agents. Such blends will normally contain from about 0.5 to 5 phr (parts per hundred parts of rubber by weight) of sulfur and/or a sulfur-containing compound with 1 phr to 2.5 phr being preferred. It may be desirable to utilize insoluble sulfur in cases where bloom is a problem.

The rubber compounds of this invention will also normally include from 0.1 phr to 2.5 phr of at least one accelerator with 0.2 phr to 1.5 phr being preferred. Antidegradants, such as antioxidants and antiozonants, will generally be included in the rubber blend in amounts ranging from 0.25 phr to 10 phr with amounts in the range of 1 phr to 5 phr being preferred. Processing oils will generally be included in the blend in amounts ranging from 2 phr to 100 phr with amounts ranging from 5 phr to 50 phr being preferred. The rubber compounds of this invention will also normally contain from 0.5

phr to 10 phr of zinc oxide with 1 phr to 5 phr being preferred. These blends can optionally contain from 0 phr to 10 phr of tackifier resins, 0 phr to 10 phr of reinforcing resins, 1 phr to 10 phr of fatty acids, 0 phr to 2.5 phr of peptizers and 0 phr to 1 phr of scorch inhibiting agents.

The silica and the organosilicon compound (silica coupling agent) will typically be mixed into the rubber blend utilizing a thermomechanical mixing technique. The mixing of the rubber formulation can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages; namely, at least one non-productive stage followed by a productive mix stage. The final curatives including sulfur-vulcanizing agents are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, silica and sulfur-containing organosilicon, and carbon black, if used, are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art. Sulfur-vulcanizable rubber composition containing a sulfur-containing organosilicon compound, a vulcanizable rubber and silica are normally subjected to a thermomechanical mixing step. This thermomechanical mixing step generally comprises a mechanical working in a mixer or extruder for a period of time suitable in order to produce a rubber temperature between 140°C and 190°C. The appropriate duration of the thermomechanical working varies as a function of the operating conditions and the volume and nature of the components. For example, conventional thermomechanical working is typically carried out for a duration of time which is within the range of about 2 minutes to about 20 minutes. It is normally preferred for the rubber blend to reach a temperature which is within the range of about 145°C to about 180°C and to be maintained at said temperature for a period of time which is within the range of about 4 minutes to about 12 minutes. In practicing this invention the need for prolonged mixing at elevated temperatures is eliminated. However, the rubber compounds of this invention will be mechanically worked until a temperature within the range of 140°C to 190°C is attained. It is normally preferred for the mixing to be carried out until a temperature within the range of about 145°C to 180°C and most preferable within the range of about 155°C to 170°C is attained. The weight ratio of the silica coupling agent to silica will typically be within the range of about 0.05:1 to about 0.3:1. The weight ratio of the silica coupling agent to silica will

preferably be within the range of about 0.1:1 to about 0.25:1. The weight ratio of the silica coupling agent to silica will more preferable be within the range of about 0.12:1 to about 0.2:1.

The rubbery polymers of this invention can be used in tire treads in conjunction with ordinary tire manufacturing techniques. Tires are built utilizing standard procedures with the rubber compositions of this invention simply being substituted for the rubber compounds, such as standard styrene-butadiene rubber, typically used in the tread rubber. After the tire has been built with the rubber composition of this invention, it can be vulcanized using a normal tire cure cycle. Tires made in accordance with this invention can be cured over a wide temperature range. However, it is generally preferred for the tires of this invention to be cured at a temperature ranging from about 132°C (270°F) to about 166°C (330°F). It is more typical for the tires of this invention to be cured at a temperature ranging from about 143°C (290°F) to about 154°C (310°F). It is generally preferred for the cure cycle used to vulcanize the tire to have a duration of about 10 minutes to about 20 minutes with a cure cycle of about 12 minutes to about 18 minutes being most preferred.

In a preferred tire the 2:1 layered silicate clay is an organophilic 2:1 layered silicate clay, wherein the silica coupling agent is present at a level which is within the range of about 0.5 phr to about 15 phr, wherein the monomer containing an amino group is 2-vinylpyridine, wherein the light weight rubber composition is further comprised of carbon black, wherein the carbon black is present at a level which is within the range of about 5 phr to about 100 phr, and wherein the amino group containing rubbery polymer contains from about 0.5 weight percent to about 5 weight percent of the monomer containing an amino group, and wherein the organophilic clay is present at a level which is within the range of about 2 phr to about 10 phr.

This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Example A

In this experiment, a block polymer, containing 2 percent 2-vinylpyridine by weight was prepared. In the procedure used, 2330 g of a silica/alumina/ molecular sieve dried premix containing 21.0 weight percent styrene and 1,3-butadiene in hexanes was

charged into a one-gallon (3.8 liters) reactor. The ratio of styrene to 1,3-butadiene was 23:77. 4.1 ml of 1M solution of N,N,N',N'-tetramethylethylene diamine (TMEDA) in hexanes and 2.0 ml of 1.03 M solution of n-butyllithium (n-BuLi) were added to the reactor to initiate the polymerization. The molar ratio of TMEDA to n-BuLi was 2:1 and the target number average molecular weight (Mn) was 240,000.

The polymerization was carried out at 75°C for 90 minutes. The GC analysis of the residual monomer contained in the polymerization mixture indicated that the polymerization was complete at this time. The polymerization mixture was cooled to 40°C. Freshly distilled 2-vinylpyridine (9.8 grams) was then added to the reactor and the polymerization was maintained at a temperature of 40°C for 5 to 10 minutes. Then, 2 ml of 1M ethanol in a solution of hexanes was added to shortstop the polymerization and polymer was removed from the reactor and stabilized with 1 phm of antioxidant. After evaporating the hexanes solvent, the resulting polymer was dried in a vacuum oven at 50°C.

The block terpolymer produced was determined to have a glass transition temperature (Tg) at –30°C. It was then determined to have a microstructure which contained 44.3 percent 1,2-polybutadiene units, 17.6 percent trans-1,4-polybutadiene units, 12.9 percent cis-1,4-polybutadiene units and 1.8% poly 2-vinylpyridine units. The Mooney ML-4 viscosity of the polybutadiene rubber at 100°C was 118.

Example B

The procedure described in Example A was utilized in these examples except that the number average molecular weight (Mn) of the 23/77 SBR was targeted at 200,000. The glass transition temperatures (Tg) and Mooney ML-4 viscosities of the resulting polybutadienes were determined to be –29°C and 100, respectively.

Example C

In this example, a pyridine end functionalized 15/85 SBR was prepared. In the procedure used, 2320 g of a silica/alumina/ molecular sieve dried premix containing 21.0 weight percent styrene and 1,3-butadiene in hexanes solvent was charged into a one-gallon (3.8 liters) reactor. The ratio of styrene to 1,3-butadiene was 15:85. Then, 1.1 ml of neat N,N,N',N'-tetramethylethylene diamine (TMEDA) and 6.8 ml of 1.03 M solution of n-butyllithium (n-BuLi) in were added to the reactor to initiate the polymerization.

The molar ratio of TMEDA to n-BuLi was 1:1 and the target number average molecular weight (Mn) was 70,000.

The polymerization was carried out at 70°C. for 60 minutes. The GC analysis of the residual monomer contained in the polymerization mixture indicated that the polymerization was complete at this time. Then, 7.0 ml of 1 M pyridine solution in hexane was added to the reactor and the reaction was continued at 70°C for 30 minutes and then 7.5 ml of 1M ethanol solution in hexanes was added to shortstop the polymerization and the polymer was removed from the reactor and stabilized with 1 phm of antioxidant. After evaporating the hexanes solvent, the resulting polymer was dried in a vacuum oven at 50°C.

The resulting functionalized SBR was determined to have a glass transition temperature (Tg) at -40°C. It was then determined to have a microstructure which contained 50 percent 1,2-polybutadiene units, 35.0 percent 1,4-polybutadiene units, and 15% polystyrene units.

Examples D and E

In this experiment, vinylpyridine-styrene-butadiene rubbers were synthesized via emulsion polymerization techniques. In the procedure used, a reactor having a capacity of 10 gallons (37.85 liters) was charged with 33.25 pounds (15.08 kg) of soft water, 16 grams. Tamol SN (sodium salt of condensed naphthalene sulfonic acid, 85 percent active), 40.0 grams tripotassium phosphate, 1046 grams of dehydrogenated rosin acid (potassium salt, 20 percent solution in water at pH 9.5) and 1911 grams of hydrogenated mixed fatty acids (sodium salt, 10 percent solution in water at pH 9.5). The pH of the solution in the reactor was adjusted to 10.2-10.8 with 10 percent sodium hydroxide. Next, to the reactor was added 23.7 grams of a solution of 82 grams water, 11.8 grams of the tetrasodium salt of EDTA and 3.0 grams of ferric sulfate heptahydrate. Then, 1638 grams of styrene and 455 grams of 2-vinylpyridine were added. Next, 27.3 grams of tert-dodecylmercaptan in 91.0 of styrene was added. The reactor was evacuated and 15.03 lbs (6.8 kg) of 1,3-butadiene was added. At 10°C, 10.3 grams of pinane hydroperoxide (44 percent active) in 91.0 grams of styrene was added. The polymerization temperature was 10°C and the agitator speed was 250 rpm. After 6 1/2 hours and about 65 percent conversion, the polymerization was shortstopped with a solution of 455 grams of water, 114 grams of the sodium salt of N,N-diethyldithiocarbamate (40 percent active) and 5.35 grams of N,N-diethylhydroxylamine

(85 percent active). After stripping off the unreacted monomers under vacuum at 120°F (49°C), a sample of the latex was coagulated and the crumb rubber dried. The coagulation was carried out by adding the latex to water containing sodium chloride and polyamine. With vigorous stirring at 160°F (71°C), 10 percent sulfuric acid was added slowly to the latex until a pH of 3-4 was reached. The rubber crumb was dried at 150°F (66°C) in a forced air oven. The Mooney viscosity of the rubber was 22. Other properties of the polymer are shown in Table 1 below.

In Example E, 1180 grams of styrene and 908 grams of 2-vinylpyridine were used and the same experimental procedure was followed as was used in Example D. Data on the resulting vinylpyridine polymers are shown in Table I.

Table I

	Example D	Example E
Approximate Composition	15S/5VP/80Bd	10S/10VP/80BD
Mooney Viscosity	22	16.5
Bound Styrene	13.7%	11.9%
Bound Vinyl Pyridine	5.7%	11.5%
Tg (DSC)	-60.5°C	-61°C

S = styrene, VP = vinyl pyridine, Bd = 1,3-butadiene

Example F

In this experiment, a rubbery terpolymer containing about 1 percent vinylpyridine, about 22 percent styrene and about 77 percent butadiene was synthesized. In the polymerization procedure employed, 33.28 pounds of soft water, 16 grams Tamol SN (sodium salt of condensed naphthalene sulfonic acid, 85 percent active), 40.0 grams of tripotassium phosphate, 1046 grams of dehydrogenated rosin acid (potassium salt, 20 percent solution in water at pH 9.5) and 1911 grams of hydrogenated mixed fatty acids (sodium salt, 10 percent solution in water at pH 9.5) were charged into a 10-gallon reactor. The pH of the solution in the reactor was adjusted to 10.2 to 10.8 with 10 percent sodium hydroxide. The pH of the solution was 10.7. Then, a solution of 455 grams water, 1.82 grams Hampene NaFe from Hamshire Chemical Co (sodium ferric ethylenediamine tetraacetate trihydrate) and 4 grams of sodium formaldehyde sulfoxylate was added to the reactor. Then, 2640 grams of styrene and 91.0 grams of 2-vinylpyridine were added. Next, 16.4 grams of tert-dodecylmercaptan in 91.0 grams of styrene was added. The reactor was evacuated and 13.64 pounds of 1,3-butadiene were

added. At 10°C, 10.3 grams of pinane hydroperoxide (44 percent active in 91.0 grams of styrene was added. The emulsion polymerization temperature was 10°C and the agitator speed was 250 rpm. After 4 hours and about 65 percent conversion, the polymerization was shortstopped with a solution of 455 grams of water, 114 grams of the sodium salt of N,N-diethyldithiocarbamate (40 percent active) and 5.35 grams of N,N-diethylhydroxylamine (85 percent active). After stripping off the unreacted monomers under vacuum at 120°F for 2 hours, a sample of the latex was coagulated and the crumb rubber dried. The coagulation was carried out by adding the latex to water containing sodium chloride and polyamine. With vigorous stirring at 160°F, 10 percent sulfuric acid was added slowly to the latex until a pH of 3-4 was reached. The rubber crumb was washed three times with water and dried at 150°F in a forced air oven. The Mooney viscosity of the rubber was determined to be 51 and it was determined to have a glass transition temperature at -52°C. The bound styrene content was determined to be 21.7 percent by FTIR and the bound vinylpyridine content was determined to be 1.5 percent from Carlo Erba nitrogen analysis. The glass transition temperature was determined by DSC (Differential Scanning Calorimetry) and is the onset glass transition temperature.

High Strength, Modulus, and Elongation Nanocomposites

Comparative Example 1 – Examples 2 and 3

In this experiment, three rubber compositions were evaluated and compared. All three were based on 100 parts of (23/77 SBR)-b-(P(2-vinylpyridine) containing 1.8% (measured) poly 2-vinyl pyridine of Example A. The recipes were mixed in two stages in a 260 cc batch Brabender mixer at 67% capacity of the mixer. In the first stage or the non-productive stage, the block copolymer, carbon black, stearic acid, zinc oxide, aromatic oils and/or unmodified clay or Organoclays (see Table II), were mixed for 4.5 minutes at 50 RPM. The body temperature of the mixer was set at 125°C. The temperature of the mixed compounds after the first stage was recorded to 144°C. In the second or the productive stage, the non-productive compounds of the first stage were mixed with the sulfur, cure accelerators and/or activators for 2.5 minutes at 35 RPM. The mixer body temperature was set at 95°C and the temperature of the mixed compounds was measured to 110°C. The recipes for the Examples in parts are given below in Table II and Table III.

Differences in the compositions are explained. Comparative Example 1 contained 30 parts of carbon black, Example 2 contained 30 parts of carbon black and 5

parts of unmodified Na^+ Montmorillonite clay (Cloisite Na^+), and Example 3 contained 30 parts of carbon black and 5 parts of Organoclay (Cloisite 30B). Cloisite 30 B is Montmorillonite clay that was ion-exchanged with organic surfactant Methyl Tallow bis-2-hydroxyethyl ammonium chloride. The typical concentration of the organic surfactant in Cloisite 30 B is around 30 % by weight. Both clays are commercially available from Southern Clay Products.

Table II: First Stage Mixing

Ingredients	Example 1 (Comparative) Parts	Example 2 Parts	Example 3 Parts
(23/77 SBR)-b-(P(2-vinylpyridine)	100	100	100
General Purpose Tread Black (ASTM N 299)	30	30	30
Stearic Acid	3	3	3
Zinc Oxide	3	3	3
Aromatic Oil	15	15	15
Cloisite Na+ (Unmodified Clay)	--	5	--
Cloisite 30B (Organoclay)	--	--	5
Total Parts	151	156	156

Table III: Second Stage Mixing

Ingredients	Example 1 (Comparative) Parts	Example 2 Parts	Example 3 Parts
First Stage Mixed Compound	151	156	156
Rubber Makers' Sulfur	2	2	2
DPG (di phenyl guanidine)	0.4	0.4	0.4
CBS (n-cyclohexyl-2-benzothiazyl-sulfenamide)	1.6	1.6	1.6
Total Parts	155	160	160

The productive compounds from the second stage were milled and the direction of milling was recorded. Torque build-up against time was studied by curing the productive compounds in an Oscillating Disk Rheometer (ODR) at 160°C. Tensile specimens were obtained by curing sheets in a compression molding press at 160°C for 20 minutes for achieving the maximum state of cure. Tensile specimens were punched-out parallel to the mill direction and three specimens were tested per Example. Specific

Gravity of the cured sheets was measured in duplicate by the hydrostatic weighing method in which the weight of the sample was measured in air and distilled water, and the specific gravity was calculated. The results are given below in Table IV.

Table IV: Physical Properties

	Example 1 (Comparative)	Example 2	Example 3
100% Modulus (Mpa)	1.31	1.62	1.76
300% Modulus (Mpa)	6.23	6.88	6.78
Tensile Strength (Mpa)	11.2	14.9	18.9
% Elongation @ Break	432	487	600
Measured Specific Gravity	1.062	1.087	1.077

Comparison of Example 2 that contained pure Na^+ Montmorillonite Clay with Example 1 (comparative) that contained no clay, indicates that the 100 % modulus and tensile strength can be increased with the unmodified clay that did not contain any organic surfactant. Comparison of Example 3 (Organoclay Cloisite 30B) with Example 1 (comparative) that contained no clay indicates that the tensile strength and elongation can be further increased by using an organoclay containing Methyl Tallow bis-2-hydroxyethyl ammonium chloride surfactant.

Transmission Electron Microscopy (TEM) was carried out on the tested tensile specimens away from the fracture and in the plane of the specimen thickness-length on the Example 3 to understand the origin of the dramatic improvement in the tensile strength that were possible on the addition of Cloisite 30B. Several TEM micrographs showed needle like clay platelets on their edges. The platelets were of the following approximate dimensions: 100-300 nm long and 2-12 nm thick. The clay platelets were predominantly exfoliated or delaminated from its original thickness that is generally known to be around 200-300 nm or so for the available Montmorillonite family of clay. Few clay platelets of larger thickness of 36 nm were also visible, but the population of such platelets was sparse. The exfoliated clay platelets were well dispersed in the elastomer matrix.

It is not the objective of this study to quantitatively characterize the dispersion and distribution of exfoliated or delaminated clay platelets, intercalated platelets and tactoidal clay platelets (primary aggregates). It is also recognized that in practice, the

global population of clay platelets may contain all of the three categories, however, in the present work, most of the clay platelets were found to be exfoliated or delaminated in the general size ranges as mentioned above. The unmodified clays or organoclays can be used to simultaneously improve the strength and elongation of rubber articles and components such as engineered belts and a tire-side wall.

Tread Compounds with Better Rolling Resistance & Light Weight

Comparative Example 4 – Example 5

In this experiment nanocomposite compounds for utilization in tire treads that exhibit better rolling resistance were evaluated. Three examples were compared. Example 3 and 5 were compared with Example 4 (comparative). Mixing times and conditions were the same as mentioned in Examples 2 and 3. Example 4 (comparative) contained 45 parts of carbon black. Example 3 was explained previously and it contained reduced 30 parts of carbon black and 5 parts of Organoclay Cloisite 30B. Example 5 additionally contained 3 parts of 50 % active silica coupling agent Si69 over the recipe of Example 3. The comparison is provided in Table V.

Table V: First Stage Mixing

Ingredients	Example 4 (Comparative) Parts	Example 3 Parts	Example 5 Parts
(23/77 SBR)-b-(P(2-vinylpyridine)	100	100	100
General Purpose Tread Black (ASTM N 299)	45	30	30
Stearic Acid	3	3	3
Zinc Oxide	3	3	3
Aromatic Oil	15	15	15
Cloisite 30B (Organoclay)	–	5	5
SI69 on Carbon Black (50% active)	–	–	3
Total Parts	166	156	159

Table VI: Second Stage Mixing

Ingredients	Example 4 (Comparative) Parts	Example 3 Parts	Example 5 Parts
First Stage Mixed Compound	166	156	159
Rubber Makers' Sulfur	2	2	2
DPG (di phenyl guanidine)	0.4	0.4	0.4
CBS (n-cyclohexyl-2-benzothiazyl-sulfenamide)	1.6	1.6	1.6
Total Parts	170	160	163

Tensile tests were conducted on samples of Comparative Example 4 and Example 5 as previously explained. Additionally, samples for all of the examples were cured in a Rubber Process Analyzer (RPA) for 20 minutes at 160°C and dynamic properties were measured for the cured rubber samples. The physical properties are given in Table VII.

Table VII: Physical Properties

	Example 4 (Comparative)	Example 3	Example 5
100% Modulus (Mpa)	1.89	1.76	2.54
300% Modulus (Mpa)	9.04	6.78	9.99
Tensile Strength (Mpa)	17.4	18.9	15.8
% Elongation @ Break	467	600	448
RPA, Cured Tan Delta 100°C, 11HZ, 2% Strain	0.126	0.111	0.09
Measured Specific Gravity	1.106	1.077	1.083

Comparison of Example 5 (Organoclay with coupling agent) with Example 3 (Organoclay) demonstrates that both 100 % and 300 % Modulus can be increased by using the silica coupling agent. Example 5 has significant lower Tan Delta values when compared with the all carbon black comparative Example 4, which is indicative of low rolling resistance. Additionally, the specific gravity of Example 5 is 1.083 against 1.106 for comparative Example 4, which will contribute to the reduced weight of the tire-tread, again leading to even lower rolling resistance and increased fuel economy.

Transmission Electron Microscopy was again carried-out on tested samples of Example 5. The clay morphology was found to be similar to the morphology of samples of Example 3 with majority of the clay platelets being in the exfoliated state in the

similar size ranges as samples of Example 3. Also, the exfoliated platelets were well dispersed in the elastomer matrix.

Nanocomposites Containing Organoclays & Carbon Black for Treads with Better Traction & Cornering Performance

Comparative Example 6 - Examples 7 and 8

In this experiment a nanocomposite for tire tread compounds having better traction characteristics was evaluated. Three rubber compositions were compared. These were: Example 6 (Comparative, 30 parts carbon black), Example 7 (30 parts black & 5 parts Organoclay Cloisite 25A), Example 8 (30 parts black & 5 parts Organoclay Cloisite 15 A). Organoclays Cloisite 25 A and Cloisite 15 A are Montmorillonite clays from Southern Clay Products that are supplied as ion-exchanged with dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium methyl sulfate and dimethyl dehydrogenated-tallow ammonium chloride respectively. The typical % concentration of the respective surfactants on Cloisite 25A and 15 A is 32 & 41 % by weight. Table VIII and Table IX give the details of the Examples. The compounds were mixed, milled, cured and tested by similar procedures as mentioned in previous comparisons.

Table VIII: First Stage Mixing

Ingredients	Example 6 (Comparative) Parts	Example 7 Parts	Example 8 Parts
(23/77 SBR)-b-(P(2-vinylpyridine)	100	100	100
General Purpose Tread Black (ASTM N 299)	30	30	30
Stearic Acid	3	3	3
Zinc Oxide	3	3	3
Aromatic Oil	15	15	15
Cloisite 25A (Organoclay)	—	5	—
Cloisite 15A (Organoclay)	—	—	5
Total Parts	151	156	156

Table IX: Second Stage Mixing

Ingredients	Example 6 (Comparative) Parts	Example 7 Parts	Example 8 Parts
First Stage Mixed Compound	151	156	156
Rubber Makers' Sulfur	2	2	2
DPG (di phenyl guanidine)	0.4	0.4	0.4
CBS (n-cyclohexyl-2 benzothiazyl-sulfenamide)	1.6	1.6	1.6
Total Parts	155	160	160

The cured physical properties are listed in Table XIII

Table X: Physical Properties

	Example 6 (Comparative)	Example 7	Example 8
100% Modulus (Mpa)	1.31	2.01	1.89
300% Modulus (Mpa)	6.23	8.04	7.73
Tensile Strength (Mpa)	11.2	15.6	15.5
% Elongation @ Break	423	469	480
Measured Specific Gravity	1.062	1.077	1.077
RPA, Dynamic Modulus, (kPa) (Cured), 100°C, 11 Hz, 1% Strain	972	1333	1227
RPA, Tan Delta 100°C, 11 HZ, 1% Strain	0.055	0.096	0.087

Examples 7 and 8 that contained different Organoclays and 30 parts of carbon black have higher 100 % and 300 % modulus, tensile strength, and percent elongation at break, when compared with the 30 parts carbon black filled Example 6. The 300 % modulus and dynamic modulus G' of Examples 7 and 8 were higher when compared with the all carbon black reinforced Example 6 (comparative). Higher modulus is indicative of improved cornering performance of the tire (see United States Patent 5,723,530). Also, Tan Delta values for Examples 7 and 8 are higher than the all carbon black Example 6. Higher Tan Delta at these conditions is indicative of higher traction of the tire tread.

Transmission Electron Microscopy was conducted on the tested tensile specimen for the sample of Example 7 that contained Cloisite 25 A organoclay. Clay platelets

were exfoliated or delaminated and were also well dispersed in the matrix. The approximate dimensions of the clay platelets were: 100-300 nm long and 2-12 nm thick.

Nanocomposites Containing Organoclays, Silica, & Carbon Black for Treads with Better Traction & Cornering Performance

Comparative Example 9 and Example 10

In this experiment organoclay, silica and carbon black nanocomposite for tire treads having improved handling and cornering characteristics & traction were evaluated. The block copolymer (23/77 SBR)-b-P(2-vinylpyridine) of a lower Mooney viscosity (100) from Example B was used instead of the high Mooney (118) rubber that was used in previous compounding examples. Comparative Example 9 contained 10 parts of carbon black, 30 parts of silica, and 5 parts of 50 % active Si69 silica coupling agent. Example 10 additionally contained 5 parts of Cloisite 30 B organoclay and 3 parts of 50% active Si69 coupling agent was added for coupling the organoclay. The mixing was done in same equipment and for 4.5 minutes as explained in previous examples. The body temperature of the mixer was, however, set at 145°C and the dump temperatures for Examples 9 and 10 were measured to 165°C and 170°C respectively. Sheets for tensile specimens were cured for 30 minutes at 160°C.

Table XI: First Stage Mixing

Ingredients	Example 9 (Comparative) Parts	Example 10 Parts
(23/77 SBR)-b-(P(2-vinylpyridine)	100	100
General Purpose Tread Black (ASTM N 299)	10	10
Stearic Acid	3	3
Zinc Oxide	3	3
Aromatic Oil	15	15
Cloisite 30B	--	5
Huber's Silica Zeopol 8745	30	30
SI69 on Carbon Black (50% active)	5	8
Total Parts	166	174

Table XII: Second Stage Mixing

Ingredients	Example 9 (Comparative) Parts	Example 10 Parts
First Stage Mixed Compound	166	174
Rubber Makers' Sulfur	2	2
DPG (di phenyl guanidine)	0.4	0.4
CBS (n-cyclohexyl-2 benzothiazyl-sulfenamide)	1.6	1.6
Total Parts	170	178

The cured physical properties are listed in Table XIII.

The nanocomposite of Example 10 that contained organoclay, silica, and carbon black had improved modulus, strength, elongation, and dynamic modulus over the silica and carbon black containing composite. The nanocomposites containing the organoclay has made possible the simultaneous improvements in almost all of the physical properties of the compounds that are important for a tire tread. Also, the tread nanocomposites of Example 10 with higher modulus is an indicator of improved handling and cornering performance of the tire (see United States Patent 5,723,530). Higher Tan Delta for Example 10 (Organoclay) is also indicative of better traction for the tread compound.

Table XIII: Physical Properties

	Example 9 (Comparative)	Example 10
100% Modulus (Mpa)	2.26	3.63
300% Modulus (Mpa)	11.23	15.61
Tensile Strength (Mpa)	14.8	19.4
% Elongation @ Break	368	374
RPA, Dynamic Modulus, G' (kPa) (Cured), 100°C, 11 Hz, 1% Strain	1280	1477
RPA, Tan Delta (Cured) 100°C, 11 Hz, 1% Strain	0.0460	0.065

The concept of making the elastomer, organoclay, silica and carbon black nanocomposites can be extended to compositions with higher amounts of silica as well.

It must be recognized that the concept of making carbon black and organoclay nanocomposites can be extended to compounds that contain very high amounts of carbon black and/or silica . The benefits from exfoliation of the organoclays can be translated to those compounds by either substituting a large part of carbon black by organoclay and improving rolling resistance and reduced specific gravity or by adding organoclays on top of the carbon black and/or silica and thereby increasing the traction and cornering performance. Similarly, increase in flexibility & strength can be obtained for rubber articles/components such as belts and side-wall components of a tire on the addition of the organoclay as demonstrated in the previous sections

Example G

In this experiment a styrene-butadiene rubber that was functionalized with 2-vinylpyridine was synthesized via emulsion polymerization technique. In the procedure used, the target composition was: 23% styrene, 77% butadiene and 3% 2-vinyl pyridine functionality. The ingredient information is given in Table XIV. The reactor was evacuated for 30 minutes. Composition A was charged to the reactor that was equipped with 2 axial flow turbines that were set at 120 rpm and the pH was adjusted to 10.5-11.0 with potassium hydroxide. Solutions B, C, D, and E were subsequently added. The reactor was re-evacuated for several minutes. Component F was added when the mixture reached 50°F (10°C). Components of G were added at 23.5 % solids.

Table XIV

Emulsion Polymerization Recipe

Material	Activity (%)	Active Parts	Active Weight (grams)	As Is Weight (grams)	Actual Charge Weight	Units
A. Reverse Osmosis (RO) Water	100	195	3900	3900	7.29	lbs
Tripotassium phosphate	100	0.36	7.2	7.2	7.2	grams
C14-18 unsaturated fatty acid potassium salt	10	2.661	53.32	532.2	532.2	grams
Disproportionated rosin potassium salt	20	1.395	27.9	139.5	139.5	grams
Sodium naphthalenesulfonate-formaldehyde dispersion	47.5	0.192	3.84	8.08	8.08	grams
Sodium C14-16 alpha-olefin sulfonate	40	0.017	0.34	0.85	0.85	grams
B. RO Water	100	4	80	80	80	grams
Hydroxymethane-sulfinic acid monosodium salt dihydrate	76.62	0.03	0.6	0.78	0.78	grams
Ethylendiamine-tetraacetic acid, ferric sodium complex	87.17	0.01	0.2	0.23	0.23	grams
C. Styrene	100	30	600	600	600	grams
t-dodecyl mercaptan	100	0.22	4.4	4.4	4.4	grams
D. 2-Vinyl pyridine	100	3	60	60	60	grams
E. Butadiene	100	67	1340	1340	1340	grams
F. Pinane hydroperoxide	44	0.04	228.00	518.18	518.18	grams
G. RO Water	100	9	51300.00	51300.00	113.10	grams
Isopropyl hydroxylamine	15	0.055	313.50	2090.00	4.61	grams

Nanocomposites of Emulsion-SBR with 2-Vinyl Pyridine Functionality

Comparative Example 11 and Examples 12-13

In this experiment elastomer nanocomposites of emulsion-SBR with 2-vinyl pyridine functionality were prepared. Compounds were mixed with emulsion-SBR containing 3% of 2-vinyl pyridine functionality prepared as explained in Example G. Mixing was done as explained in previous compounding examples . Differences in the Examples 11 -13 are explained. Example 11 contained 30 parts of carbon black,

Examples 12 and 13 additionally contained 5 parts of Cloisite 30 B organoclay, and 5 parts of Cloisite 30B organoclay plus 3 parts of SI69 (50 % active) respectively. The recipe information is given in Table XV and Table XVI.

Table XV: First Stage Mixing

Ingredients	Example 11 (Comparative) Parts	Example 12 Parts	Example 13 Parts
Emulsion-SBR (3% 2-Vinyl Pyridine)	100	100	100
General Purpose Tread Black (ASTM N 299)	30	30	30
Stearic Acid	3	3	3
Zinc Oxide	3	3	3
Aromatic Oil	15	15	15
Cloisite 30B (Organoclay)	-	5	5
SI69 on Carbon Black (50% active)	-	-	3
Total Parts	151	156	159

Table XVI: Second Stage Mixing

Ingredients	Example 11 (Comparative) Parts	Example 12 Parts	Example 13 Parts
First Stage Mixed Compound	151	156	159
Rubber Makers' Sulfur	2	2	2
DPG (di phenyl guanidine)	0.4	0.4	0.4
CBS (n-cyclohexyl-2 benzothiazyl-sulfenamide)	1.6	1.6	1.6
Total Parts	155	160	163

Table XVII: Physical Properties

Ingredients	Example 11 (Comparative)	Example 12	Example 13
100% Modulus (Mpa)	2.2	3.2	3.6
300% Modulus (Mpa)	9.67	12.7	14.3
Tensile Strength (Mpa)	15.9	24	23.8
% Elongation @ Break	424	479	451
RPA, Dynamic Modulus, G' (kPa) (Cured), 100°C, 11 Hz, 1% Strain	1365	1482	1678

In Example 12 that contained Cloisite 30B organoclay, there was an increase in the 100% modulus, 300% modulus, tensile strength, elongation, and dynamic modulus over the comparative Example 11. In Example 13 that additionally contained Si69 coupler, the 100% modulus, 300% modulus, and dynamic modulus were further increased, and the increased level of tensile strength was largely maintained. Both Examples 12 and 13 that have increased modulus over the all carbon black containing control Comparative Example 4, are indicative of better handling and cornering performance of the tire.

Variations in the present invention are possible in light of the description of it provided herein. While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. It is, therefore, to be understood that changes can be made in the particular embodiments described which will be within the full intended scope of the invention as defined by the following appended claims.

WHAT IS CLAIMED IS:

1. A rubber composition that is comprised of: (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, and (2) from about 0.1 phr to about 25 phr of a 2:1 layered silicate clay.

2. A rubber composition as specified in claim 1 wherein the 2:1 layered silicate clay is an organophilic 2:1 layered silicate clay.

3. A rubber composition as specified in claim 2 wherein said composition is further comprised of a silica coupling agent.

4. A rubber composition as specified in claim 3 wherein said amino group containing rubbery polymer contains from about 0.5 weight percent to about 10 weight percent of the monomer containing an amino group, wherein the composition contains from about 1 phr to about 10 phr of the organophilic 2:1 layered silicate clay, and wherein the silica coupling agent is present at a level which is within the range of about 0.5 phr to about 15 phr.

5. A rubber composition as specified in claim 3 wherein said amino group containing rubbery polymer contains from about 0.5 weight percent to about 10 weight percent of the monomer containing an amino group, wherein the composition contains from about 1 phr to about 10 phr of the organophilic 2:1 layered silicate clay, and wherein the ratio of the silica coupling agent to the 2:1 layered silicate clay is within the range of about 0.1:1 to about 1.5:1.

6. A rubber composition as specified in any preceding claim wherein the monomer containing an amino group is a pyridyl group containing vinyl compound.

7. A rubber composition as specified in any one of claims 1-5 wherein the monomer containing an amino group is selected from the group consisting of 2-vinylpyridine and 4-vinylpyridine.

8. A rubber composition as specified in any preceding claim wherein the light weight rubber composition is further comprised of carbon black, and wherein the carbon black is present at a level which is within the range of about 5 phr to about 100 phr.

9. A rubber composition as specified in any preceding claim wherein the amino group containing rubbery polymer contains from about 1 weight percent to about 4 weight percent of a monomer containing an amino group.

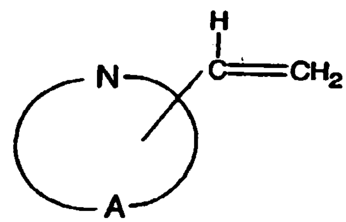
10. A rubber composition as specified in claim 4 wherein the organophilic clay is present at a level which is within the range of about 1 phr to about 7 phr and wherein the silica coupling agent is present at a level which is within the range of about 1 phr to about 5 phr.

11. A rubber composition as specified in claim 3 wherein said rubber composition is further comprised of about 1 phr to about 70 phr of silica.

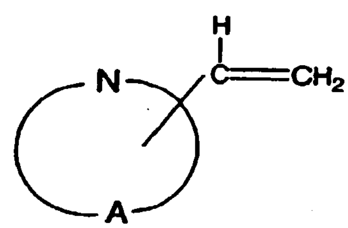
12. A rubber composition as specified in claim 2 wherein the organophilic 2:1 layered silicate clay was modified with up to about 70 part by weight of a quaternary ammonium salt surfactant selected from the group consisting of methyl tallow bis-2-hydroxyethyl ammonium halides, methyl tallow bis-2-hydroxyethyl ammonium alkyl sulfates, methyl tallow bis-2-hydroxyethyl ammonium nitrate, methyl tallow bis-2-hydroxyethyl ammonium hydroxide, methyl tallow bis-2-hydroxyethyl ammonium acetate, methyl tallow bis-2-hydroxyethyl ammonium phosphate, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium halides, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium alkyl sulfates, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium nitrate, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium hydroxide, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium acetate, dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium phosphate, dimethyl dehydrogenated-tallow ammonium halides, dimethyl dehydrogenated-tallow ammonium alkyl sulfates, dimethyl dehydrogenated-tallow ammonium nitrate, dimethyl dehydrogenated-tallow ammonium hydroxide, dimethyl dehydrogenated-tallow ammonium acetate, and dimethyl dehydrogenated-tallow ammonium phosphate.

13. A rubber composition as specified in any preceding claim wherein the 2:1 layered silicate clay is selected from the group consisting of smectite, montmorillonite, saponite, beidellite, hectorite, fluorohectorite, bentonite, nontronite, laponite, vermiculite, and hallosite.

14. A rubber composition as specified in claim 2 wherein the amino group containing rubbery polymer is comprised of repeat units that are derived from an amino group containing monomer selected from the group consisting of (a) heterocyclic amine having the structural formula:



wherein A represents a -CH- group or a $-CH_2-$ group and wherein the heterocyclic amine is aromatic or aliphatic and (b) derivatives thereof heterocyclic amine having the structural formula:



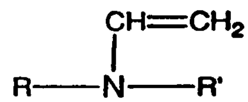
wherein A represents a -CH- group or a $-CH_2-$ group and wherein the heterocyclic amine is aromatic or aliphatic.

15. A rubber composition as specified in claim 3 wherein the silica coupling agent is present at a level which is within the range of about 2 phr to about 4 phr.

16. A rubber composition as specified in claim 8 wherein the carbon black is present at a level which is within the range of about 25 phr to about 75 phr.

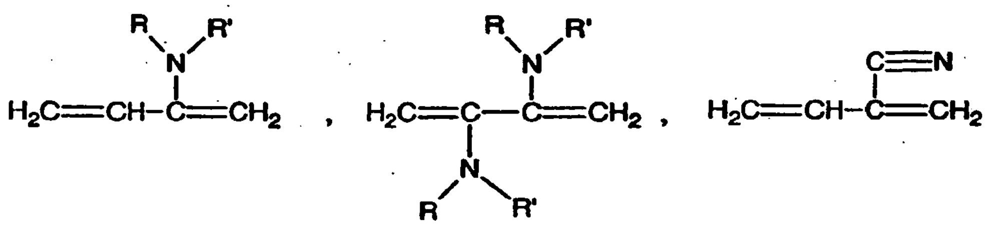
17. A rubber composition as specified in claim 2 wherein the amino group containing rubbery polymer is comprised of repeat units that are derived from an amino group containing monomer selected from the group consisting of (a) N-vinyl 2-

pyrrolidone, (b) N-vinyl caprolactam, and (c) N-vinyl dialkyl amines having the structural formula:

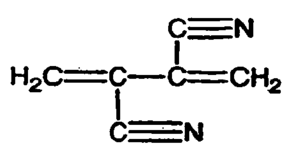


wherein R and R' can be the same or different and represent alkyl groups that contain from 1 to about 10 carbon atoms.

18. A rubber composition as specified in claim 2 wherein the amino group containing rubbery polymer is comprised of repeat units that are derived from an amino group containing monomer that is a conjugated diolefin that is substituted with amino and/or cyano groups which is selected from the group of compounds of having the structural formula:



and



wherein R and R' can be the same or different and represent alkyl groups that contain from 1 to about 10 carbon atoms.

19. A tire which is comprised of a generally toroidal-shaped carcass with an outer circumferential tread, two spaced beads, at least one ply extending from bead to bead and sidewalls extending radially from and connecting said tread to said beads; wherein said tread is adapted to be ground-contacting; wherein the tread is comprised of: (1) an amino group containing rubbery polymer, wherein said amino group containing rubbery polymer contains from about 0.1 weight percent to about 20 weight percent of a monomer containing an amino group, (2) from about 0.1 phr to about 25 phr of a 2:1 layered silicate clay, and (3) a silica coupling agent.

20. A tire as specified in claim 19 wherein the 2:1 layered silicate clay is an organophilic 2:1 layered silicate clay, wherein the silica coupling agent is present at a level which is within the range of about 0.5 phr to about 15 phr, wherein the monomer containing an amino group is 2-vinylpyridine, wherein the light weight rubber composition is further comprised of carbon black, wherein the carbon black is present at a level which is within the range of about 5 phr to about 100 phr, and wherein the amino group containing rubbery polymer contains from about 0.5 weight percent to about 5 weight percent of the monomer containing an amino group, and wherein the organophilic clay is present at a level which is within the range of about 2 phr to about 10 phr.

21. A rubber composition substantially as hereinbefore described in Examples 2, 3, 5, 7, 8, 10, 12 and 13.

22. A tire which is comprised of a generally toroidal shaped carcass with an outer circumferential tread, two spaced beads, at least one ply extending from bead to bead and sidewalls extending radially from and connecting said tread to said beads; wherein said tread is adapted to be ground contacting; wherein the tread is comprised of a rubber composition substantially as hereinbefore described in Examples 2, 3, 5, 7, 8, 10, 12 and 13.

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Application No:	GB 0127546.0	**Examiner:**	Martin Price
Claims searched:	1-22	**Date of search:**	16 April 2002

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Other: Online - WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 848754 (Phillips) - see eg Examples I and II	1 at least
X	EP 0551532 A1 (Nippon) - see eg claims 1, 2, 7, 8	1 at least
X	US 5576373 (Exxon) - see eg example 3	1 at least
X	US 4889885 (Toyota) - see eg the claims and examples	1 at least
X	US 3973071 (PPG) - see eg Table I and examples	1 at least
X	US 2885381 (Phillips) - see eg the examples	1 at least
X	WPI Accession number 2001-018708[03] & JP 2000159960 (Kanegafuchi) - see abstract	1 at least
X	WPI Accession number 1980-44156C[25] & JP 55062269 (Teijin) - see abstract	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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